

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Exploring the self-organization in nano-confined ionic liquids: simultaneous micro-Raman and micro-XRD experiments.	Experiment number: SC 3322
Date of experiment: from: 24 may 2012 to: 28 may 2012	Date of report: 1 march 2013
Local contact(s): Michael Reynolds, Manfred Burghammer	<i>Received at ESRF:</i>

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Report: This experiment consisted in the simultaneous use of confocal micro-Raman and microfocused X-ray (SAXS) scattering for the *in situ* characterization of the sol-gel chemistry when precursor silica particles reacted with a carboxylic acid while dissolved in an imidazolium ionic liquid. The resulting gels constitute a new class of materials also known as *ionogels*, with properties of interest for applications in catalysis, fuel cells, and Li-ion batteries, as a few examples.

The aim of this pioneering experiment was to elucidate the role of the ionic liquid in the sol-gel process, an unexplored issue so far. While the Raman spectra give proof of the evolving chemical reaction, the recorded SAXS patterns contain details on the evolving local structure inherent of both the ionic liquid and the growing silica network. The collected data are still being analyzed, even though the current analysis has revealed the following interesting features.¹

Even though the ionic liquid used in the synthesis (1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide: C_6C_1TFSI , see Fig. 1) exhibits a nanostructuration in its bulk form,² our SAXS data show that this nano ordering is lost at mixing (*i.e.* in the sol) and is then slowly recovered as the reaction proceeds (Fig 2). Interestingly we can observe that the characteristic correlation lengths associated to the polar and non-polar domains increase and decrease, respectively as the sol-gel reaction proceeds, eventually approaching plateau values at the point of gelation, t_{gel} (Fig 3). This evolution, observed here for the first time, suggests a breathing of the ionic liquid's nano structure (Fig. 4), which we believe is associated to the preferential sites of reactants and products as a consequence of polarity differences.³ The

¹ The results are under analysis and intended for submission to the journal *Chemistry of Materials*.

² A. Martinelli, M. Maréchal, Å. Östlund, J. Cambedouzou, *PCCP*, 2013, doi: C3CP00097D.

³ Tetramethyl orthosilicate particles will prefer to be close to the hydrophobic alkyl chains while reaction products like methanol or methyl formate will reside in the polar regions.

structural evolution observed by this SAXS experiment is also consistent with previously reported NMR spectra showing that the relative chemical shifts of the imidazolium protons ($\Delta\delta_{\text{H}}$) evolve and correlate to the point of gelation.⁴

Our results indicate that ionic liquids are potentially capable to orient reactants with very important implications with respect to their use as, for instance, microreactor sites. Nevertheless, the loss in local order observed with $\text{C}_6\text{C}_1\text{TFSI}$ in the sol also suggest that longer chained imidazolium ionic liquids (*e.g.* with C_{10} , C_{12} , C_{14} , etc) may be more robust and so also capable to act as structure directing agents for the growing silica network. In fact, the ionogels obtained with $\text{C}_6\text{C}_1\text{TFSI}$ seem to be amorphous,⁵ while the use of $\text{C}_{10}\text{C}_1\text{TFSI}$ (or longer chains) may impart an order on the silica network at the nanometer scale, similarly to the case of zeolites. Such a finding will strengthen the potentiality of ionic liquids as surfactants/structure directing agents to control the porous structure of the resulting silica gel,⁶ thus opening for new interesting application fields (such as in catalysis) and also simplifying conventional synthesis procedure.⁷

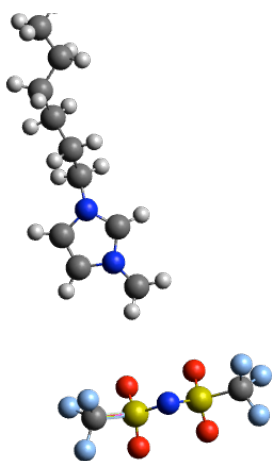


Fig 1. Molecular structure of the ionic liquid $\text{C}_6\text{C}_1\text{TFSI}$.

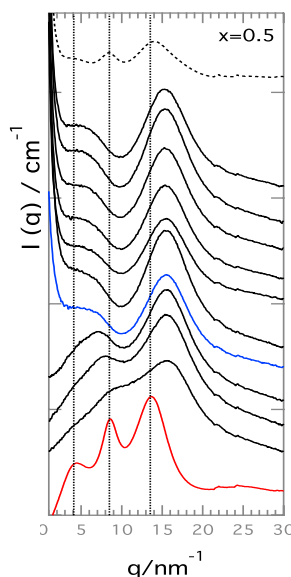


Fig 2. SAXS patterns recorded *in situ*: bulk ionic liquid (red), sol-to-gel (black), aged ionogel (dotted). The blue trace corresponds to the gelation time.

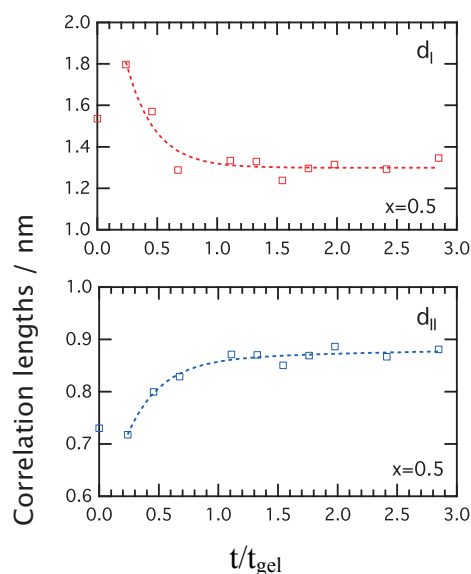


Fig 3. Real space correlation lengths for the non-polar domains (red) and polar domains (blue) as a function of t/t_{gel} reduced time.

⁴ A. Martinelli and L. Nordstierna, *PCCP*, 2012, **14**(38): 13216-23.

⁵ As from ongoing TEM analyses.

⁶ F. Michaux *et al.*, *Langmuir*, 2012, **28**(50): 17477-17493.

⁷ Being non-volatile, ionic liquids allow for the so called *ionothermal* synthesis, feasible at low temperatures and with no need of high-pressure autoclaves.

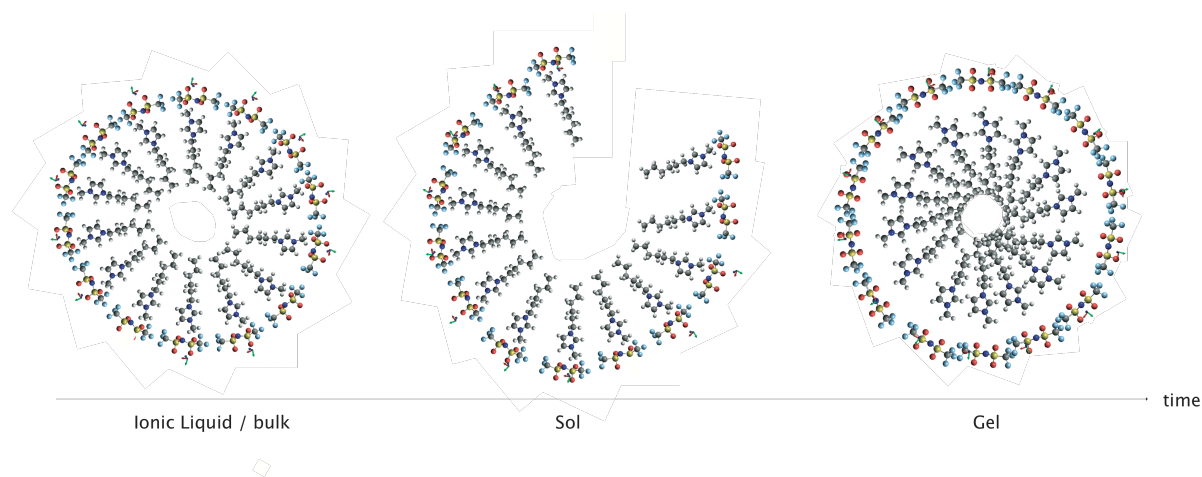


Fig 4. Proposed schematic diagram for the ionic liquid's nanostructural evolution as a function of time.

We therefore wish to follow up our successful experiment at the ID13, and propose to characterize the sol-gel process by micro-Raman and SAXS simultaneously when the ionic liquid $C_{10}C_1TFSI$ is used as a cosolvent for the reaction of tetramethyl orthosilicate and formic acid. We strongly believe that this new experiment will further clarify on the role of ionic liquids in mesostructured silica and, consequently, broaden the frontiers for their potential use.

In view of this new experiment, we will construct an own capillary holder, as well as adjust both the ionic liquid content and the relative amount of acid to slow down the gelation time and so allow for an increased number of collected data points.⁸

⁸ If compared with the previously performed experiment (Exp. No. SC 3322).